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Calculation of ground state energy, lowest π-π^* energies and the first ionisation potential of transbutadiene using a non-perturbative many-body theory for open-shell systems

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In a recent publication by the present authors Mukherjee *et al* (1975), a non-perturbative many-body formulation for open-shell atomic and molecular systems was developed, which utilized an Ursell-type Cluster expansion of the total wavefunction about a suitably chosen model space spanned by a set of degenerate (or near-degenerate) determinantal wavefunctions. In his communication we have widened the scope of application of this theory, by including within the model space functions belonging to N and N-1 particle subspaces. The calculations then yield the ground state correlation energy, the lowest singlet and triplet energies and the first ionization potential of a N-electron system. The theory has been tested on a 4π-electron problem, transbutadiene, with excellent results.

1. INTRODUCTION

Recently, we have presented[1,2] a non-perturbative many—body theory for calculating the correlation energy of open-shall atomic and molecular systems. The formulation utilizes the Ursell type cluster representation of the exact wavefunction about a suitable linear combination of degenerate (or near degenerate) determinantal wavefunctions. We were led to an effective Hamiltonian for the system, consisting only of linked terms, which acting entirely within the the subspace of the trial wavefunctions yields the energy eigenvalues of the system. The theory was tested for the case of the lowest π—π^* singlet and triplet energy states of the molecule transbutadiene, with excellent results.

This non-perturbative open shell theory, which we shall henceforth refer to as NPOST, has far more general implications. Since the theory uses the the language of second quantization, there is no inherent limitation on the number of particles the system may possess. It is possible, therefore, to include in the set of model space functions those belonging to both N and N—1 particle systems. The resulting effective Hamiltonian then yields energies both for the N and N—1 particle systems Furthermore the functions in the model space need not be degenerate at all It is thus possible to obtain *through a single calculation* the ground state energy and the excited state energy and the excited states of the N-particle system, as also the corresponding quantities for the N $\pm$ 1 particle systems. By taking a suitable difference, one obtains the ionization potential of the N particle systems, or the electron affinity of the N — 1 particle system. The accuracy of the computed ionization potential and electron affinity reflects the accuracies in the energies of the individual states, whose difference is being considered. There exist of course, alternative method like the technique of Green's function, which yield the ionization potential directly. The present method is more general in the sense that in addition to giving the ionization potential, it can yield both the ground and excited states energies of the N and N $\pm$ 1 particle systems.

In the preset communication we shall illustrate some of these points by demonstrating a calculation of ionisation potential, ground and lowest π—π^* energies of the molecule transbutadience. Let us first recall the essential features of the NPOST.

Resume of NPOST

Let us define a model space of determinantal function $\Phi_1, \Phi_2, \ldots\ldots\Phi_n$, in terms of which let us define a set of trial functions Ψ_0^k,

$$\Psi_0^k = \sum_i^n C_i^k \quad \Phi_i \tag{1}$$

We may then express the corresponding true wavefunctions Ψ^k as

$$\Psi^k = \exp(\hat{T})\ \Psi_0^k, \tag{2}$$

where $\hat{T}$ has the form

$$\hat{T} \sum_p \hat{T}_p \tag{3a}$$

$$\hat{T}_p = \frac{1}{(p!)^2} \sum \langle EFGH \ldots I \mid t_p \mid ABCD \ldots I \rangle_R\ X^+_K\ X^+_F \ldots X^+_J\ X_I \ldots X_H\ X_A \tag{3b}$$

From the Schrodinger equation

$$H \psi^k = E^k \psi^k \tag{4a}$$

or $$He^{t} \psi_0^{k} = E^k e^{t} \psi_0^{k} \tag{4b}$$

we get $$U_L \Psi_0^k = E^k \Psi_0^k \tag{4c}$$

where U_L has the form[1,2]

$$U_L = \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{\substack{l_1 R_m \\ =T_1 \ldots T_n}} \sum_{\substack{k_1, k_2 \\ k_1+k_2=m}} (-1)^{k_2} (R_n R_{m-1} \ldots$$

$$K_1 \text{ objects } (\langle 0 | H | 0 \rangle + F + V) R_1 R_2 \ldots K_2 \text{ objects })_L . \tag{5}$$

where $H = \langle 0 | H | 0 \rangle + F+V$, written in normal order.

The matrix elements of the operators T_n are obtained by projecting eq. 4(c) on to the excited determinantal states Φ^*_i lying outside the model space. We then get a set of simultaneous equations

$$\langle \Phi^*_e | U | \Phi_i \rangle = 0, \text{ for all } i \neq e. \tag{6}$$

whose solutions give the matrix elements of T_n. The energies are now determined by diagonalising the matrix $[\langle \Phi_i | U_L | \Phi_j \rangle]$.

All the calculations are facilitated by utilizing a diagrammatic representation of U_L. It is necessary to classify the orbits into groups of hole, valence and particle states. We shall not elaborate these notions here, as they are described in great detail in references 1, 2 where the proof of eq.. (5) is also to be found.

2. The Ionization Potential the Ground State and the Lowest π—π^* Energies of Transbutadiene

As a test of the utility of the NPOST for calculating these quantities, we have considered the same system as considered by us earlier[1,2] namely, transbutadiene, in the π-electron approximation. This model system consists of four π-electrons moving in an effective field of the core, and as basis we take the eight molecular spin-orbitals built out of the four atomic π-orbitals centered on the four carbon atoms in the molecule. We designate these molecular orbitals in order of increasing orbital energies as $1, \bar{1}, 2, \bar{2}, 3, \bar{3}, 4, \bar{4}$ where the bar indicates reversed spin. The single determinant ground configuration of transbutdiene is the state $\Psi_0^1 \equiv \Phi_1 = A \mid 1\, \bar{1}\, 2\, \bar{2} \mid$, A being the normalized antisymmetrizer. The first approximate singlet and triplet excited

states are described by the combinations

$$\Psi_0^2 = \frac{1}{\sqrt{2}}(\Phi_2+\Phi_3)$$

and

$$\Psi_0^3 = \frac{1}{\sqrt{2}}(\Phi_2-\Phi_3)$$

with $\Phi_2 = A|1\ \bar{1}\ 2\ 3|$ and $\Phi_3 = A|1\ \bar{1}\ 3\ \bar{2}|$ and the approximate ionized configurations are $\Psi_0^4 = \Phi_4 = A\ |\ 1\ \bar{1}\ 2\ |$ and $\Psi_0^5 = \Phi_5 = A\ |\ 1\ \bar{1}\ \bar{2}\ |$. We take the two particle state $A\ |\ 1\ \bar{1}\ |$ as the vacuum state $|\ 0\ >$, and hence, according to the criteria mentioned in he preceding section, 1, $\bar{1}$ are hole states 2, $\bar{2}$, 3, $\bar{3}$ are valence states and 4, $\bar{4}$ are particle states. In order to test how a single calculation can reproduce the correlation energy of the care part let us also include the vacuum $|0>$ in the model space. We call it $\Psi_0^6 = \Phi_6$. We accordingly have

$$\Phi_1 = N[\gamma^+_2\ \gamma^+_{\bar{2}}]|0>,\quad \Phi_2 = N[\gamma^+_2\ \gamma^+_3]|0>,\quad \Phi_3 = N[\gamma^+_{\bar{2}}\ \gamma^+_{\bar{3}}]|0>$$

$$\Phi_4 = \gamma^+_2|0> \qquad \Phi_5 = \gamma^+_{\bar{2}}|0> \qquad \Phi_6 = |0>$$

We must now consider all the t_p -matrix elements in the operator $\hat{T}$ which correlate successively the core state $A\ |\ 1\ \bar{1}\ |$ the ground state $A\ |\ 1\ \bar{1}\ 2\bar{2}|$ the ionized states $A\ |\ 1\ \bar{1}\ 2\ |$ and $A\ |\ 1\ \bar{1}\ \bar{2}\ |$ and the states Ψ_0^2 and Ψ_0^3. In the given basis we have seven, twentyeight and twentyfour distinct matrix elements of T_p which correlate the core, the ground, the excited states and the ionic states respectively. As many of these configurations are energetically degenerate, many of the T_p -matrix elements may be set pairwise equal a priori, and this considerably reduces the dimension of the set of simultaneous equations to be solved.

In the present calculation we have confined ourselves to the linear approximation, which makes the whole problem computationally tractable, and at the same time is sufficient to demonstrate the power of the NPOST. The diagrammatic conventions are identical to those followed in references 1 and 2 where all the relevant details of classifying the U_L -diagrams into G-blocks are to be found. Eqs. (6) are then solved to find the values of the T-matrix elements.

The U_L -diagrams which contribute to the energies may be classified in the following manner. All closed diagrams having no external lines contribute to the correlation energy of the core state $A\ |\ 1\ \bar{1}\ |$. The diagrams which contribute to the correlation energy of the ground state of the molecule are (a) the closed diagrams, (b) diagrams having one ingoing and one outgoing valence line labelled 2 or $\bar{2}$, and (c) diagrams with two ingoing valence lines labelled 2 and $\bar{2}$ and two outgoing valence lines with the same labels. For the

energies of the singlet and triplet states we have to consider the diagonal terms $\langle \Phi_2 | U_L | \Phi_2 \rangle$ and $\langle \Phi_3 | U_L | \Phi_3 \rangle$ and the off-diagonal term $\langle \Phi_2 | U_L | \Phi_3 \rangle$. In the diagonal terms the contributory blocks are respectively (1) the closed diagrams (2) diagrams having one ingoing and one outgoing line both labelled 2, $\bar{2}$, 3, $\bar{3}$ and (3) diagrams with two incoming valence lines labelled 2 and $\bar{3}$ (or 3 and $\bar{2}$) and two outgoing valence line labelled similarly. In the off-diagonal terms the only contributory diagrams are those having two outgoing lines labelled 2, $\bar{3}$ and two incoming valence lines labelled 3 and $\bar{2}$.

And finally the diagrams which contribute to the energy of the state $A\,|1\,\bar{1}\,2|$ are the closed diagrams and diagrams having one incoming and outgoing valence line labelled 2.

All these energies are calculated and the ionization potential is obtained as the difference of the energies of the 4-particle and 3-particle correlated ground configurations. In addition we also obtain the energies of the first π—π^* singlet and triplet energy levels of transbutadiene. The correlation energy of the core comes from the closed diagrams only. Hence a *single* T-operator is found to furnish the energies of various states, The results are discussed in the following section.

3. Results and discussions

The P-P-P parametrization used by Cizek and Sroubkova[3] has been adopted in constructing the core and two-particle integrals in the π-electron basis. We have performed a Hartree-Fock calculation for the state $|1\,\bar{1}\,2\,\bar{2}|$ to generate the occupied and unoccupied molecular orbitals. For testing the performance of the present theory we have found out the model exact answers in the basis of the given configurations, through configuration interaction calculations for all the states whose energies are being considered. We have confined ourselves to the linear approximation in that we have included in U_L terms containing first power in $\hat{T}$ only. The results of the calculations are summarized in the following table.

Table 1

Energies of various states in eV	Present Theory	Configuration interaction
Ground State energy	−90.4831	−90.5114
Lowest π-π^* singlet energy	−83.9691	−83.9629
Lowest π-π^* triplet energy	−86.8499	−86.8256
First Ionization potential	11.6327	11.6830

A perusal of this table shows that even in the linear approximation the present theory yields excellent results. This shows the predictability of the theory to describe simultaneously different type of states.

References

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